

Tritium: A MicroPower Source for On-Chip Applications

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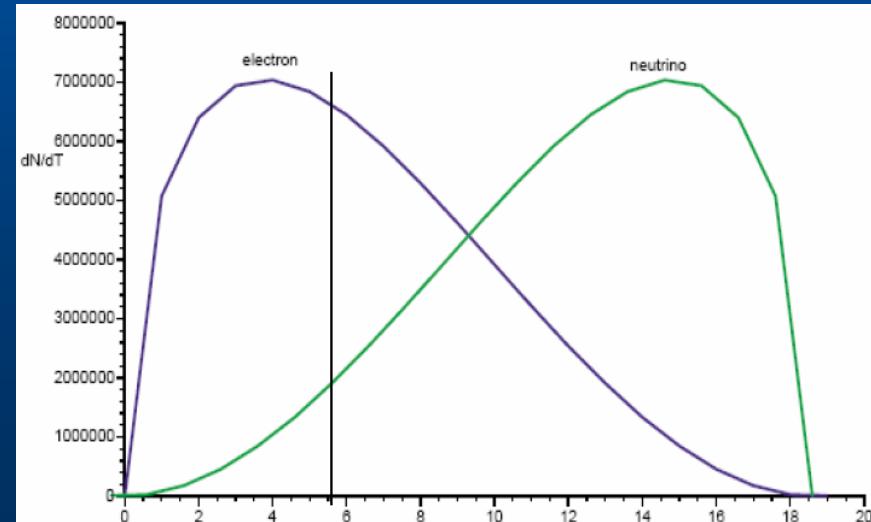
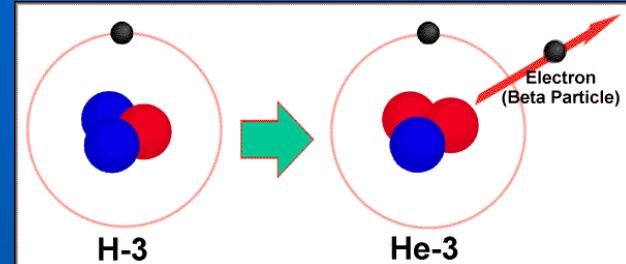
Endorsed by National Hydrogen Association and Society for Advancement of Material and Process Engineering

Outline

- **Tritium: Basics**
- **Tritium: A MicroPower Source**
 - Beta-Voltaics
 - Beta-Powered MEMS
 - Beta-Luminescence
 - Cold Electron Source
- **Tritium: A Characterization/Diagnostic Tool**
 - Tritium Tracer Studies
 - Tritium Effusion Studies
 - Defect Dynamics
 - Particle Sensor Applications
- **Summary**

Tritium

- Isotope of Hydrogen
- ${}^3\text{H} \rightarrow {}^3\text{He}^+ + \beta^- + \bar{\nu}_e + 18.6 \text{ keV}$
- Nuclear Half-life: $t_{1/2} = 12.32 \text{ years}$
 $\lambda = 1.78 \times 10^{-9} \text{ s}^{-1}$
- Activities: $1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$
 $1 \text{ Ci} = 0.39 \text{ std cc}$
 $1 \text{ Ci} = 33.7 \mu\text{W}$
- Biological: Half-life: 10 days
ALI*: 80 mCi
 - *Annual Limit on Intake
- Chemically: Identical to ${}^1\text{H}$
Mass effect (~3amu)
Beta catalysis
- Range (max): 4.5 – 6 mm in air
5 – 7 micron in water

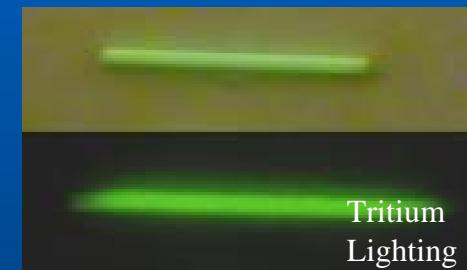
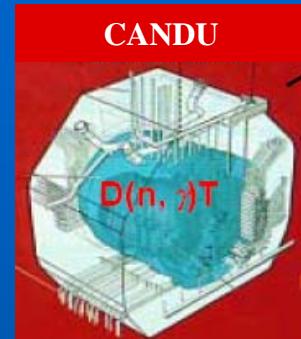


Producers & Users

- Producers of Tritium

- Ontario Power Generation (OPG)
 - ~1 kg/year
- Korean Electric Power Company (KEPCO)
- USA
 - 225 kg produced since 1955
 - 12-75 kg stockpiled
- Russia
- India, Pakistan

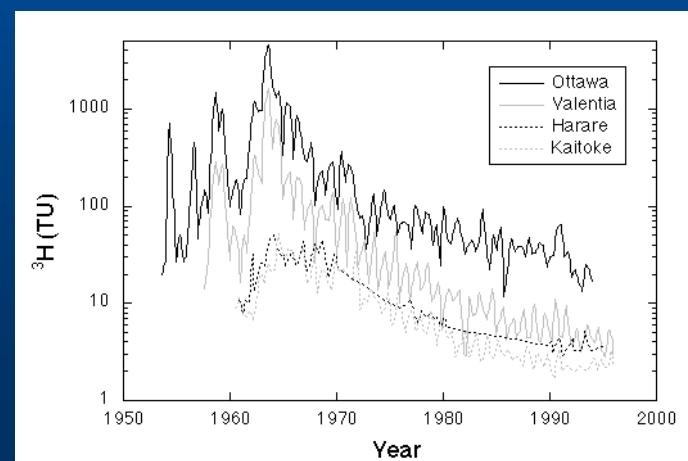
Tritium Producing Burnable Absorber Rods (TPBARs)
(Lithium Rods in a Light Water Reactor)



- Users of Tritium

- Pharmaceutical Research (~100g)
- Tritium Lighting Industry (~30g)
- Fusion Studies
 - Magnetic Confinement (ITER ~40g)
 - Inertial Confinement
- Other

Tritium in
Natural Waterways



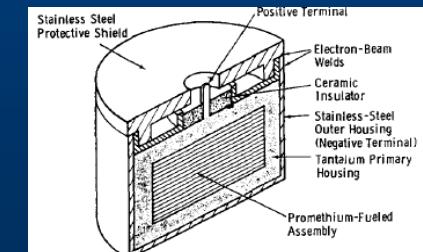
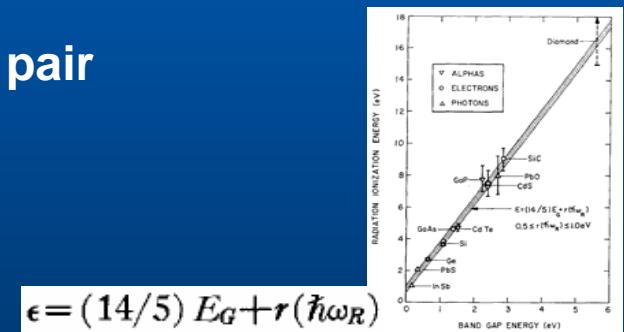
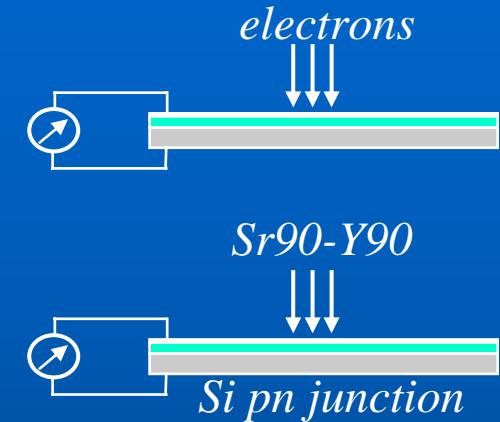
$$1 \text{ Tritium Unit (TU)} = 1 \text{ T} : 10^{18} \text{ H}_4$$

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 - Tritium Outgassing & Effusion Studies
 - Defect Dynamics
 - Particle Sensor Applications
- Summary

BetaVoltaics

- 1951, Ehrenberg, Lang, & West:
 - Electron-voltaic effect (on a Se device)
- 1956, Rappaport
 - First direct conversion betavoltaic device (planar configuration, 0.4% efficiency)
- 1968, Klein
 - Band-gap dependence of electron-hole pair (ehp) generation by ionizing radiation
- 1974, Olsen
 - Theoretical treatment of betavoltaic conversion efficiencies for a variety of semiconductor materials
- 1970s, D W Douglas Laboratories
 - Planar silicon betavoltaics fueled with ^{147}Pm
 - Efficiencies ranged in 0.7 to 2%



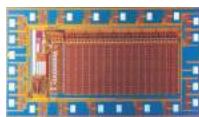
Renewed Interest in Radioisotope Batteries

- **Continual miniaturization of electronic and electromechanical systems**
 - Decreased power consumption
- **Integrated Power Sources (SoC)**
- **High energy densities compared to chemical batteries**
- **Operation in extreme environments**
 - For example, temperatures of -100 to +150 °C

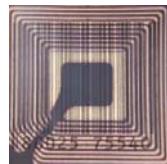
MicroPower Applications

Sensor/Memory Chips

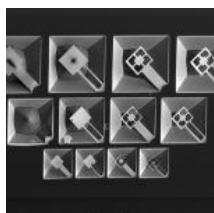
Power requirement: 1-10 μW



Non-volatile Memory



RF-ID tag



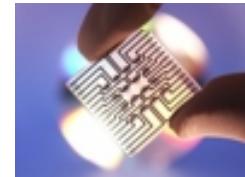
Electrostatic actuation
of MEMS/NEMS

SoC Microsystem

Power requirement: 1-10 mW



Chip-scale
atomic clock



Micro-gas
Analyzer

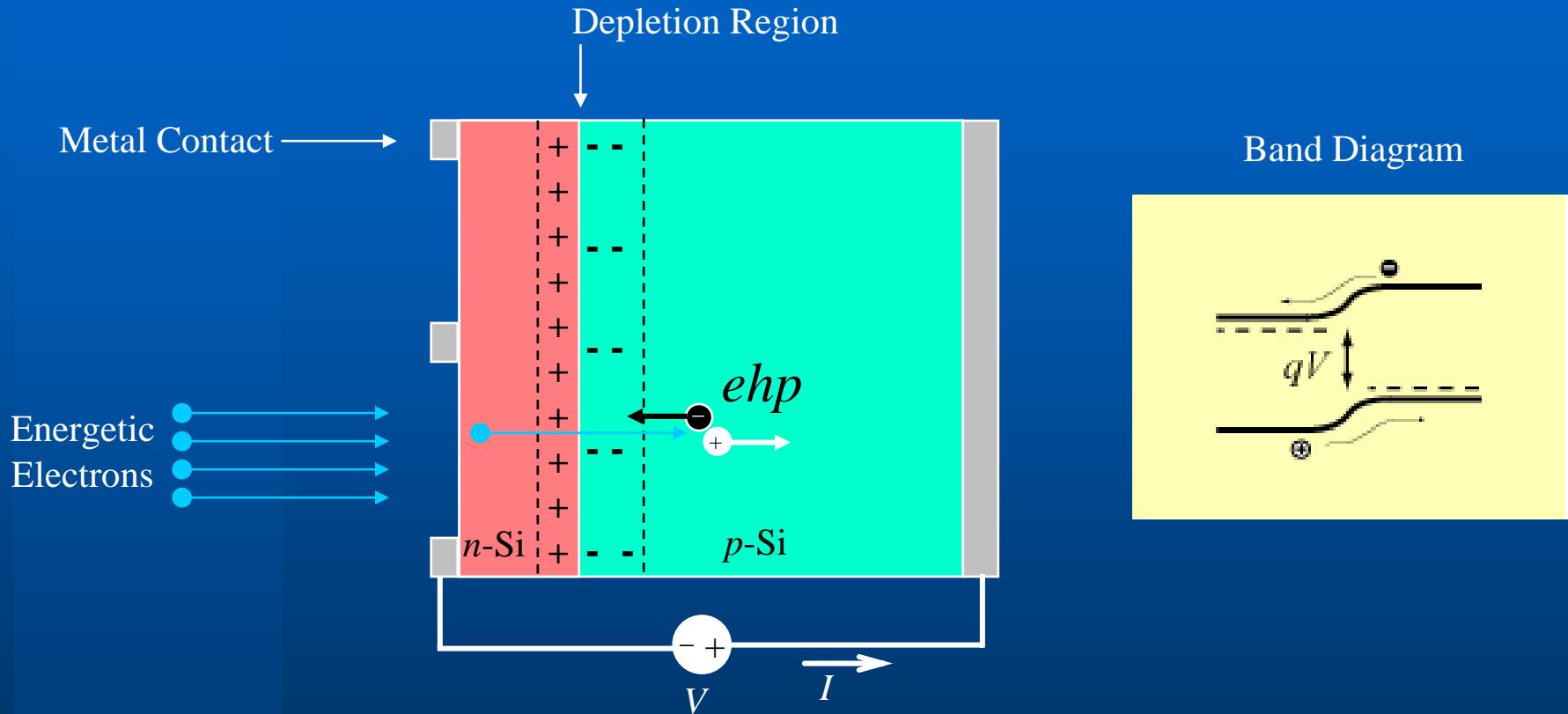


Chip-scale
Navigation system

Market

- All Batteries: \$50 billion
- Target markets for betavoltaic batteries
 - Oil, gas, and environmental
 - Military
 - Medical
 - Space
 - Emerging MEMS/NEMS
- Market for betavoltaics \$1 billion +

Electron/Beta Voltaics



ehp: electron-hole pair

Choice of Radioisotope

Isotope	E _{avg} (keV)	E _{max} (keV)	P (W/g)	Work (kWh/ 4y/g)	T _{1/2} (yrs)
H-3	5.7	18.6	0.34	10.3	12.3
Ni-63	21	66	0.07	2.5	92
Sr-90	540	900	0.75	25	28
Pm-147	62	230	0.34	7.3	2.6

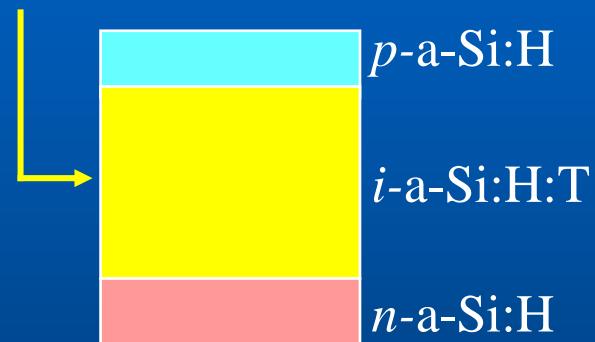
Tritium

- Low energy β- emitter (benign radioisotope)
- Low cost: \$2.5-\$4/Ci
- Long enough lifetime
- Can be immobilized in a solid matrix
- On-chip integration
- Mature (existing tritium lighting industry)

Intrinsic Tritiated Amorphous Silicon Betavoltaic Device

- Substitute tritium for hydrogen in hydrogenated amorphous silicon *pin* photovoltaic devices
- Tritium within the energy conversion layer
 - In contrast to betas originating from a source external to the device
- Volume source battery
 - Attained through stacking of many cells
 - In contrast to a planar surface source battery

Tritiated Intrinsic Layer (uniform)



a-Si:T Betavoltaic Device

At $t \sim 0$

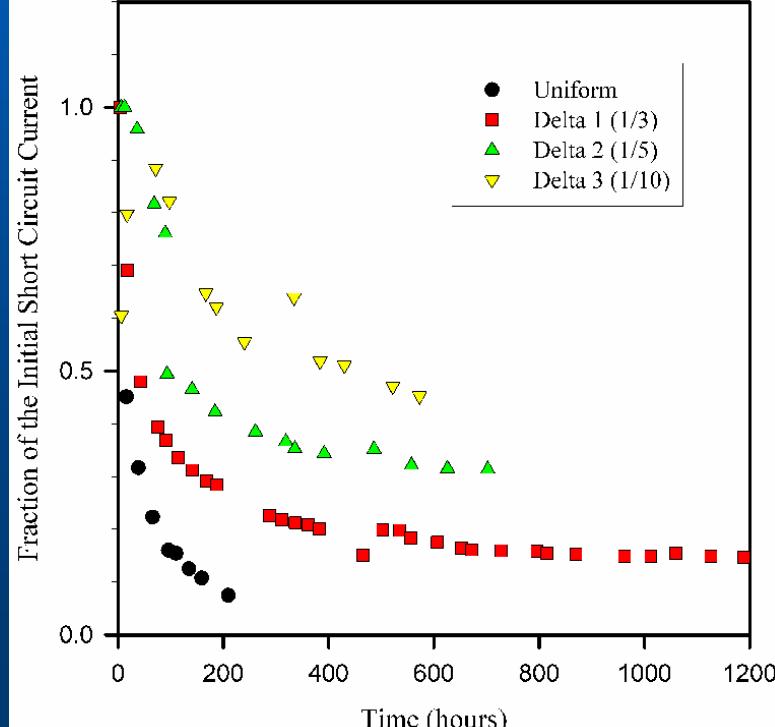
$$I_{sc} = 0.98 \text{ nA}$$

$$V_{oc} = 21 \text{ mV}$$

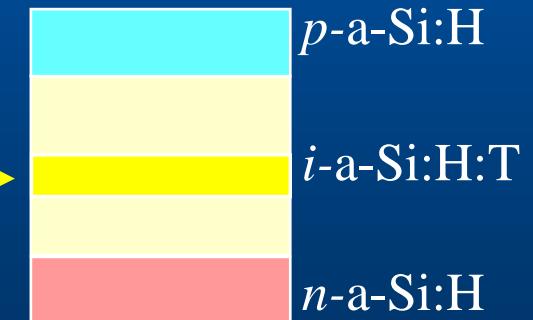
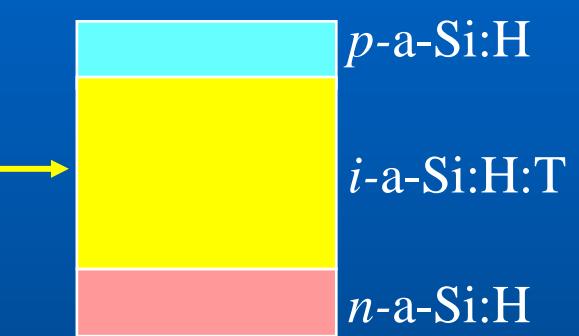
$$\eta = 0.1\%$$

At $t \sim 10 \text{ days}$

$$I_{sc} < 0.1 \text{ nA}$$



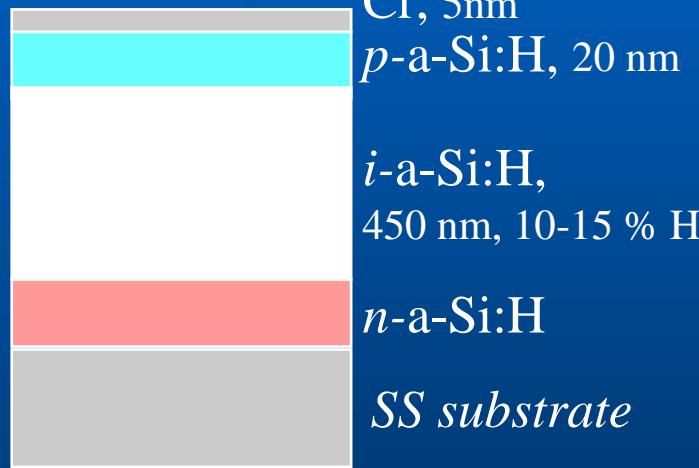
**Tritiated
Intrinsic Layer (uniform)**



**Tritiated
Delta Layer**

a-SiH Betavoltaic Cell Powered by T₂ Gas

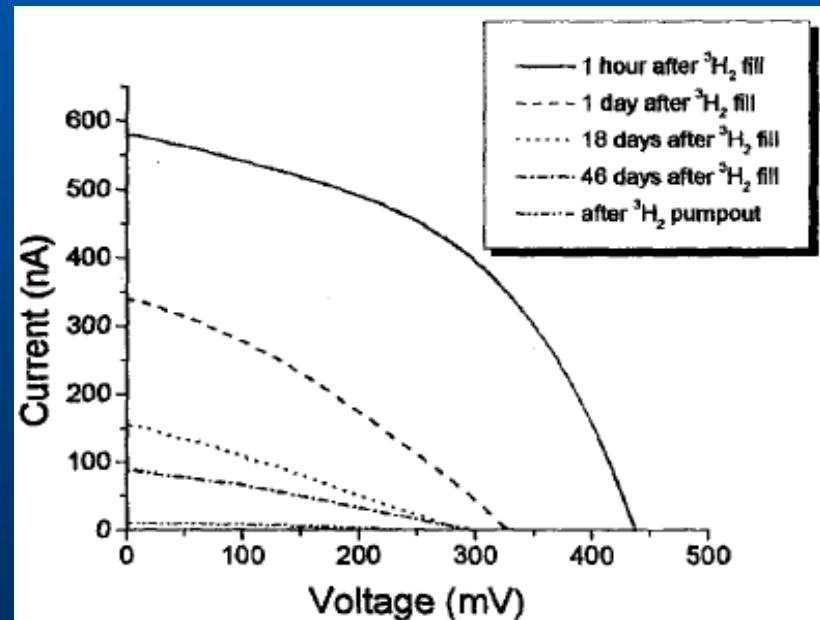
a-SiH Betavoltaics with ultrathin contact



Tritium gas
pressure: 678 torr

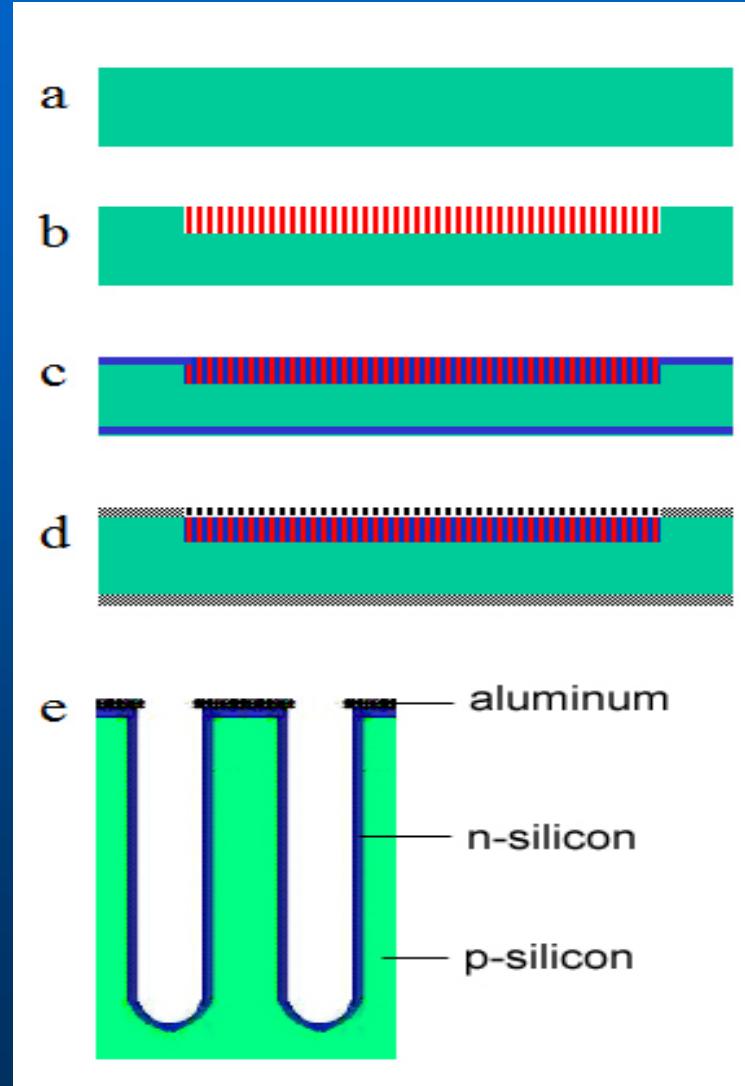
At $t \sim 0$
 $I_{sc} = 637 \text{ nA/cm}^2$
 $V_{oc} = 457 \text{ mV}$
 $\eta = 1.2\%$

At $t \sim 46 \text{ days}$
 $\eta < 0.1\%$

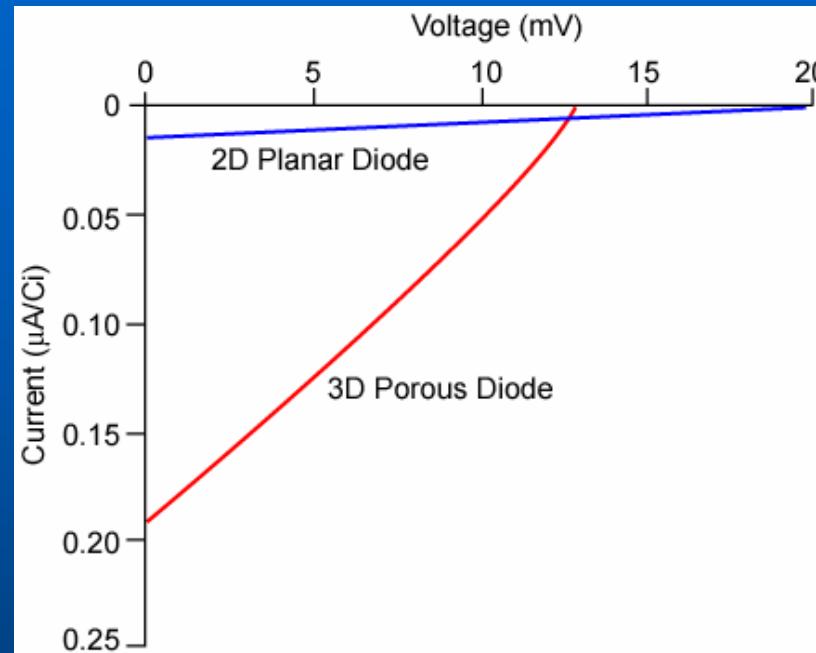
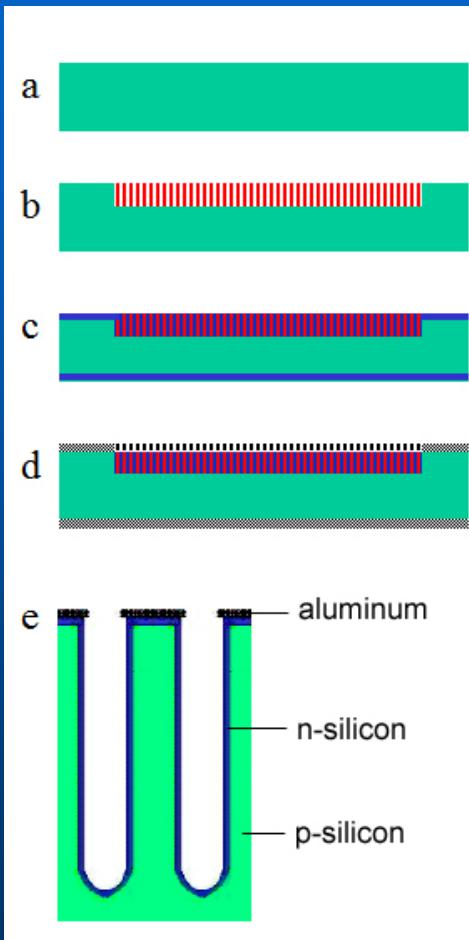


Porous Silicon 3D Betavoltaics

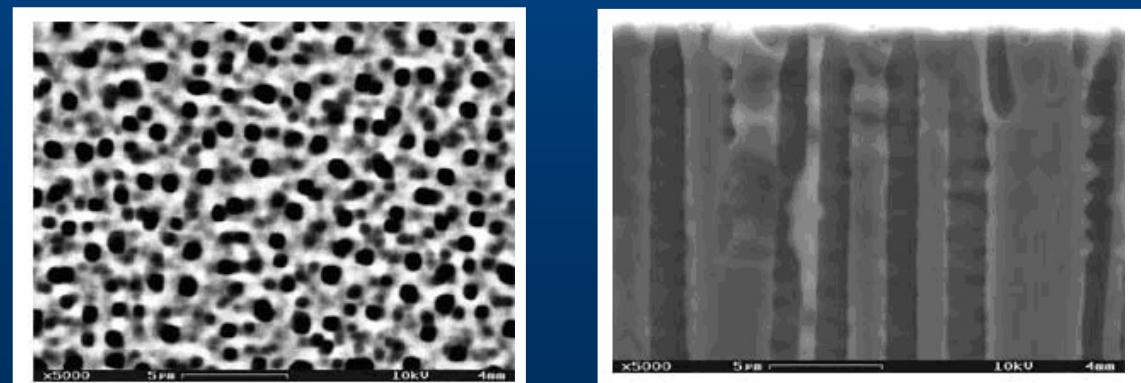
- Introduce micropores in silicon through electrochemical anodization
- Create *pn* junction in the pores through diffusion of n-type dopant
- Introduce an appropriate radionuclide in the pores
- A Volume Source Battery



3D Versus 2D Betavoltaics

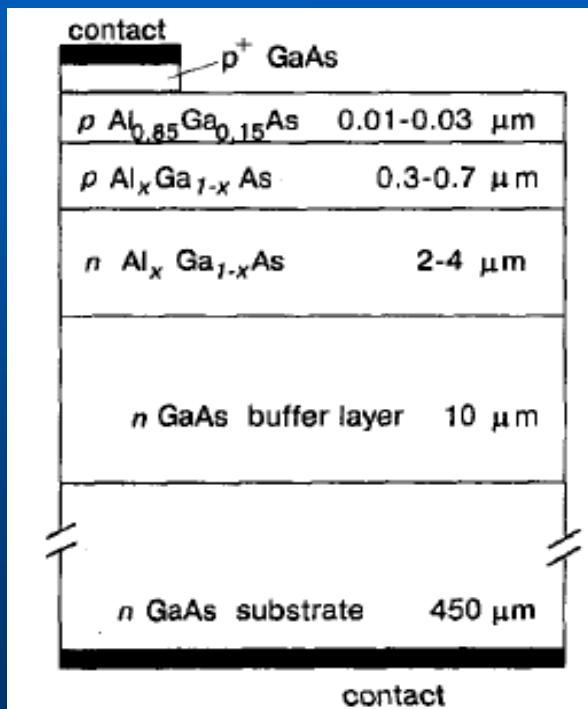


$$\eta_{2D} = 0.02\%$$
$$\eta_{3D} = 0.2\%$$



III-V Betavoltaics

AlGaAs/GaAs Heterojunction Betavoltaics



Source of betas	Generated current density, $\mu\text{A}/\text{cm}^2$	Open circuit Voltage, V	Output Power, $\mu\text{W}/\text{cm}^2$	Efficiency (%)
Tritium-titanium	0.04	0.75	0.024	5.6
Tritium gas	0.76	0.91	0.55	5.8
Tritium green lamp	0.12	0.78	0.074	---

Silicon Carbide Betavoltaics

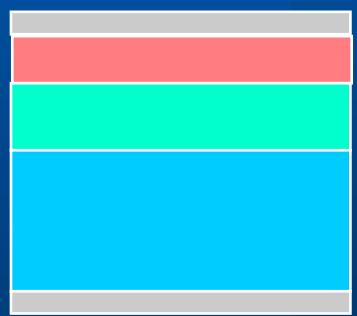
4H SiC BV Cell

1 mCi, ^{63}Ni Source (66keV)

$$I_{sc} = 16.8 \text{ nA/cm}^2$$

$$V_{oc} = 0.72 \text{ V}$$

$$\eta = 6\%$$



Chandrashekhar, Thomas, Li, Spencer, Lal,
Appl. Phys. Lett., **88** (2006) 033506

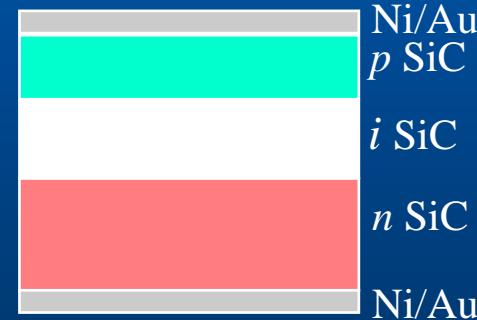
4H SiC *pin* BV Cell

8.5 GBq, ^{33}P Source (249 keV)

$$I_{sc} = 2.1 \mu\text{A/cm}^2$$

$$V_{oc} = 2.04 \text{ V}$$

$$\eta = 4.5\%$$



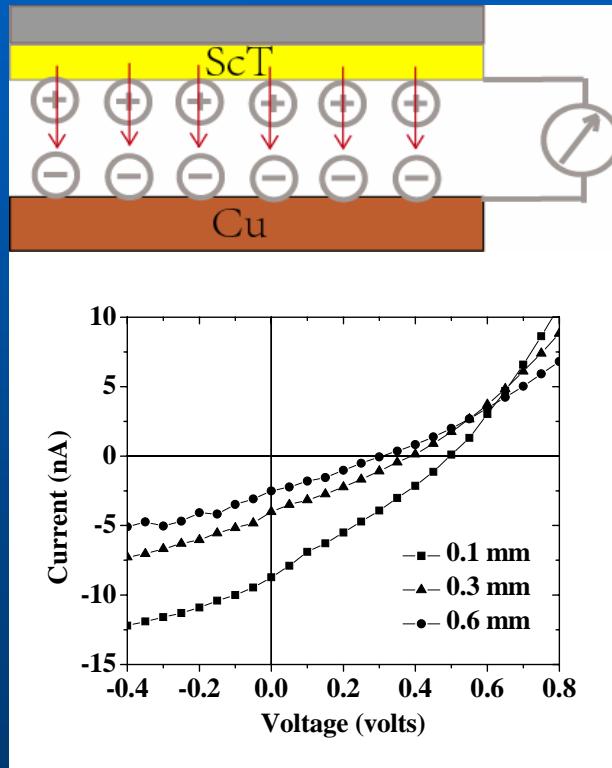
Eiting, Krishnamoorthy, Rodgers, George, Robertson,
Brockman, *Appl. Phys. Lett.*, **88** (2006) 064101.

Contact Potential Difference Betavoltaics

Air-medium CPD BV

$$I_{sc} = 2.7 \text{ nA/cm}^2$$

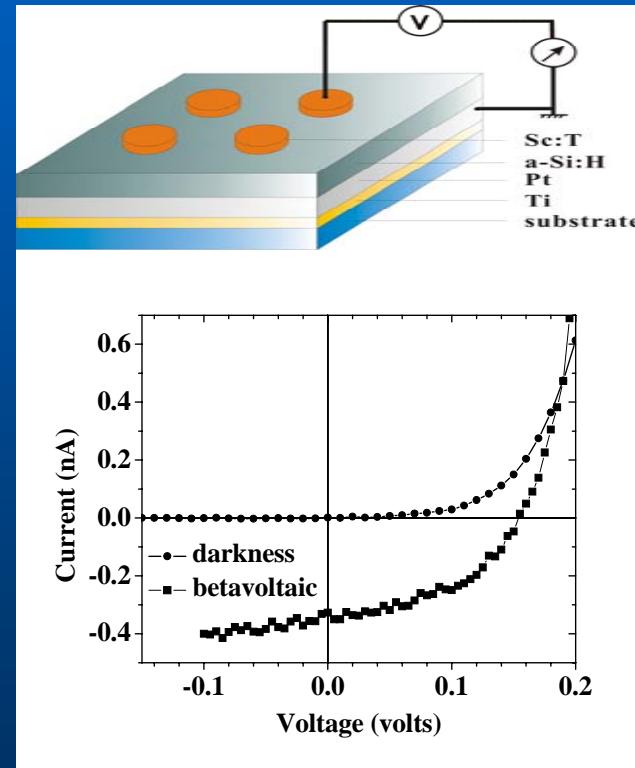
$$V_{oc} = 0.5 \text{ V}$$



Solid CPD BV

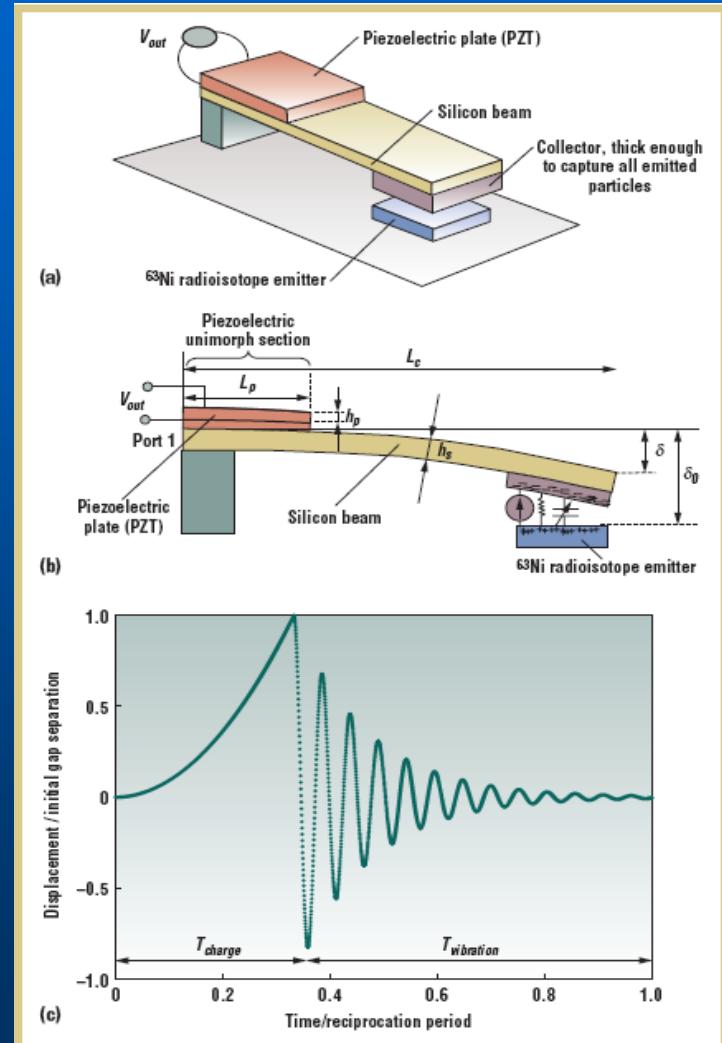
$$I_{sc} = 5.3 \text{ nA/cm}^2$$

$$V_{oc} = 0.16 \text{ V}$$



MEMS: Radioisotope-Powered Piezoelectric Generator

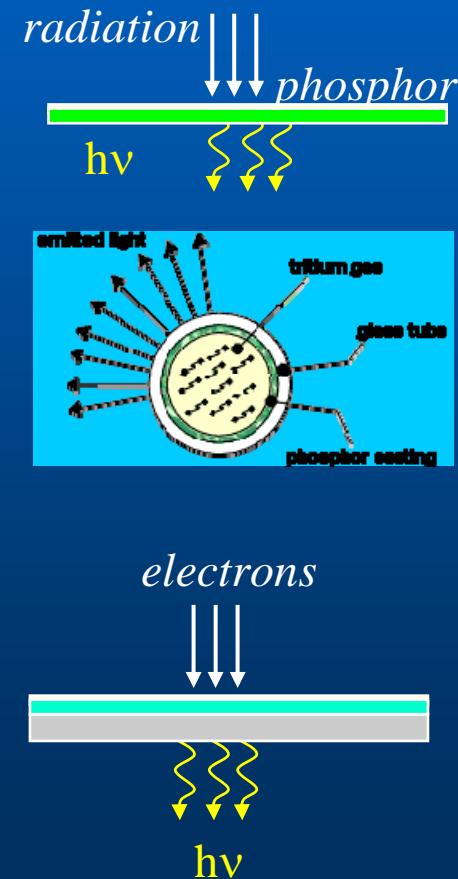
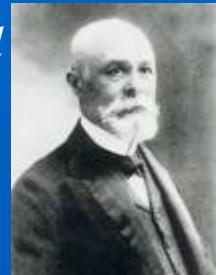
- Self-reciprocating direct-charging cantilever
- Direct conversion of collected-charge-to-motion energy into electrical
 - Radioisotope kinetic energy stored in the cantilever
 - Piezoelectric generator converts stored mechanical energy into electrical energy
- Overall efficiency 2.78%



BetaLuminescence

- 1898, Becquerel
 - Radioluminescence
 - Phosphorescence material: potassium uranyl sulphate
- 1920s, Elster, Geitel, and Cookers
 - Alpha radiation induced scintillations in ZnS.
- 1967, International Atomic Energy Agency (IAEA)
 - Standards for the use of common RL sources.
 - Most common: tritium beta-luminescence
- Present
 - Tritium gas lighting
 - Radium ZnS:Cu paint
 - Novel materials & technologies in Betaluminescence
 - Organic
 - all-organic formulation: polystyrene and fluorescent dye
 - organic system with inorganic phosphor
 - Inorganic
 - semiconductor pn junctions
 - incorporation of tritium in solid matrix:
amorphous materials, hydrides, carbon nanotubes, zeolites

Becquerel



Cold Electron Source

- **Tritium immobilized in a solid**
- **Materials**
 - **Tritiated metal tritides**
 - **Tritiated amorphous silicon**
 - Plasma enhanced chemical vapour deposition: entire film
 - Tritiation post film deposition: ~50 nm
 - **Tritiated silica on Si-chip**
 - High pressure tritium loading
 - Laser irradiated locked tritium
 - **Tritiated silicon**
 - High pressure tritium loading
 - Surface region: ~ 10 nm
 - **Tritiated carbon nanotubes**

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Tritium Tracer Technique

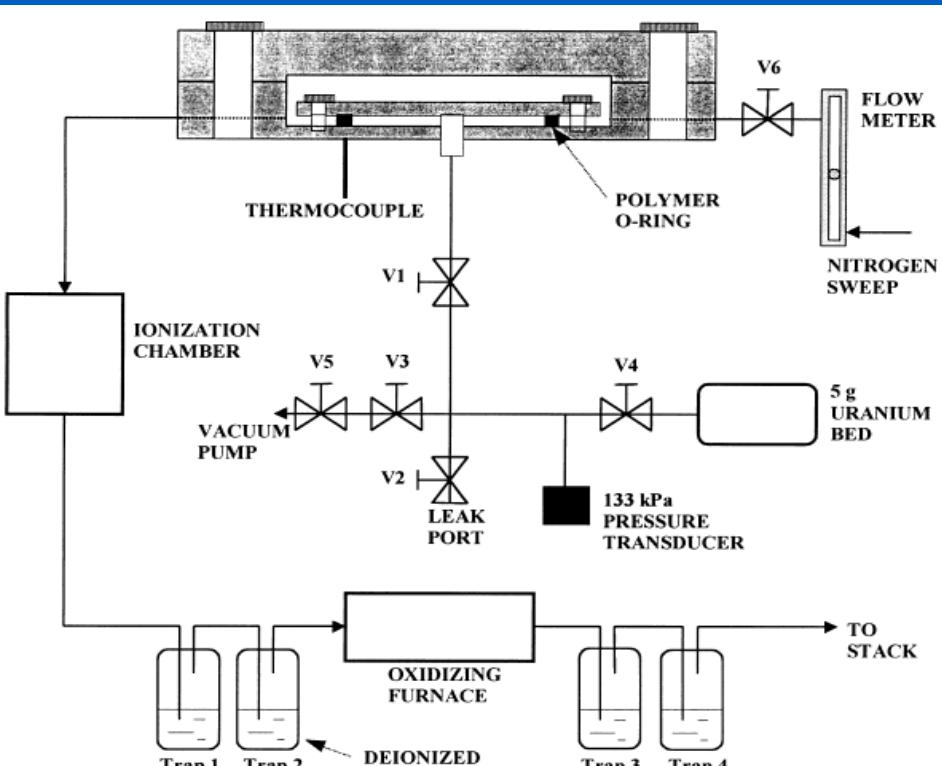
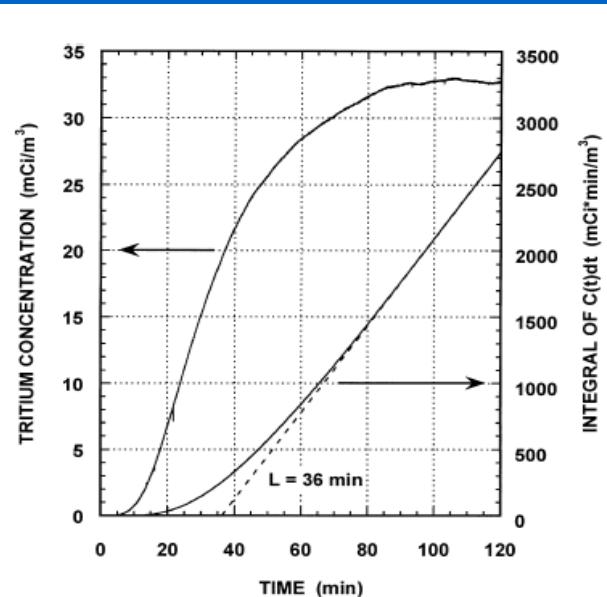


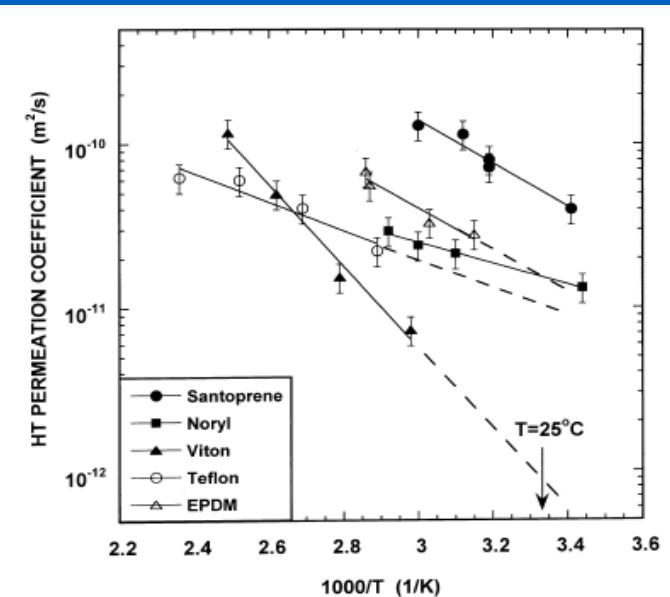
Fig. 1. Schematic of the experimental loop.

- Tritium as a tracer in measurement of hydrogen permeation in polymer for selection of new material in hydrogen fuel cell.
- Two diagnostics to trace permeating HT: an ionization chamber tritium detector and an HTO water trap/copper oxide furnace/HTO water trap system
- Tritium radiotracer method: simple, effective, reliable.

Tritium Tracer Technique (cont'd)



Characteristic permeation curve
for Noryl at 60 °C



Arrhenius plot of tritium permeation
for the five polymers

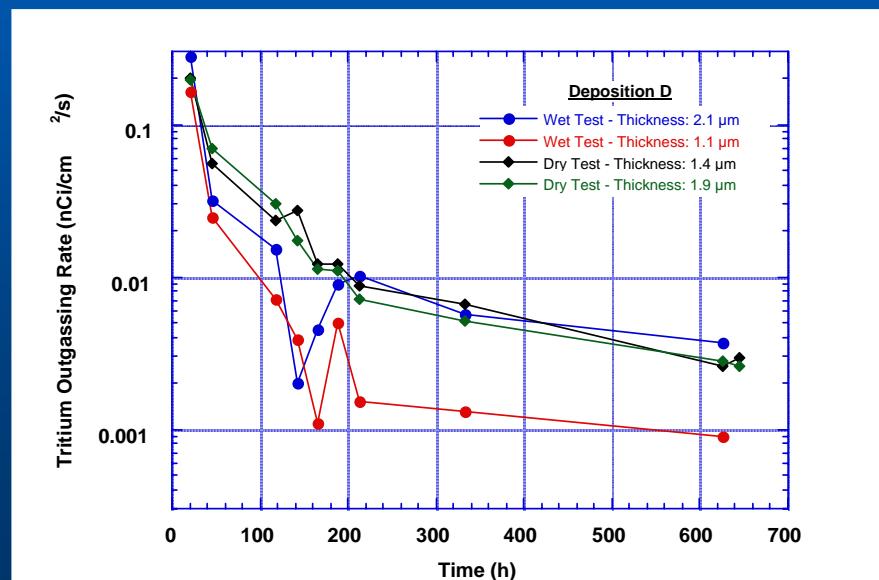
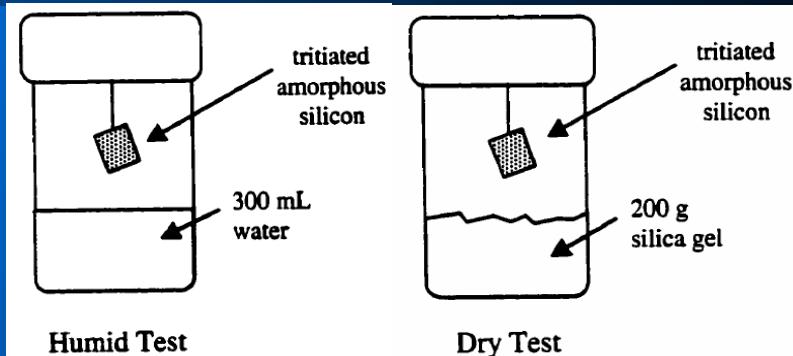
- Materials Tested: EPDM, Teflon, Viton, Santoprene and Noryl
- Permeation Parameters in reasonable agreement with referenced values of H, D, T

Stodilka, Kherani, Shmayda, Thorpe,
Intl. J. Hydrogen Energy **25** (2000) 1129-1136

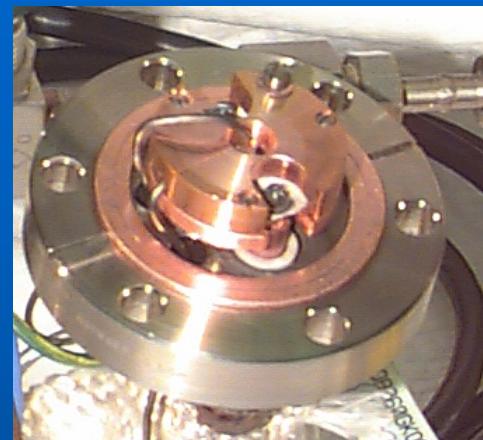
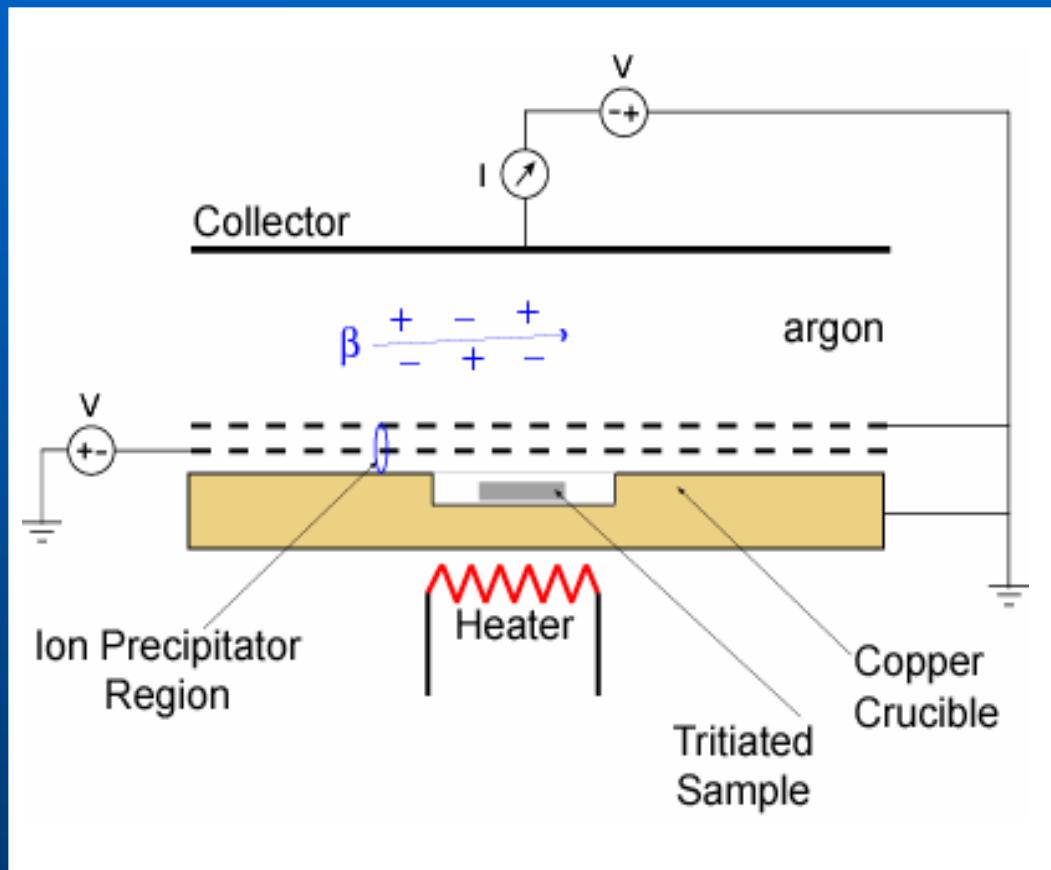
Polymer	Temperature (°C)	P_0^{b}	E_P^{c}	D_0^{b}	E_d^{c}
Viton	63–129	1.72×10^{-4}	47.7	2.22×10^{-5}	29.1
Teflon	74–150	8.38×10^{-9}	16.7	1.39×10^{-7}	14.9
EPDM	44–76	2.74×10^{-7}	24.4	3.50×10^{-5}	27.9
Santoprene	20–60	1.21×10^{-6}	25.1	1.36×10^{-5}	21.2
Noryl	18–70	2.11×10^{-9}	12.3	4.05×10^{-7}	16.9

Tritium Outgassing Studies

- A tool to study hydrogen stability in materials
- High sensitivity
 - Difficult-undetectable for the inactive H-isotope using conventional methods
- Dry and wet test
 - Absorption of HTO desorbed from surface of a given sample
- Tritiated amorphous silicon at room temperature
 - Atomic T concentration: 9%
 - Asymptotic evolution: $2 \times 10^8 \text{ atmcm}^{-2}\text{s}^{-1}$
 - Equivalently: Void-Network H diffusion half-life of 60 years
 - This is for a low H stability material, owing to the high void fraction of the material

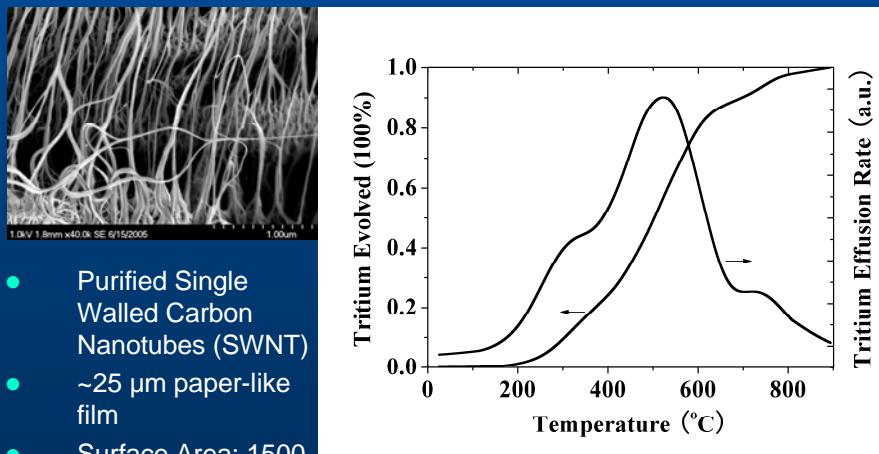
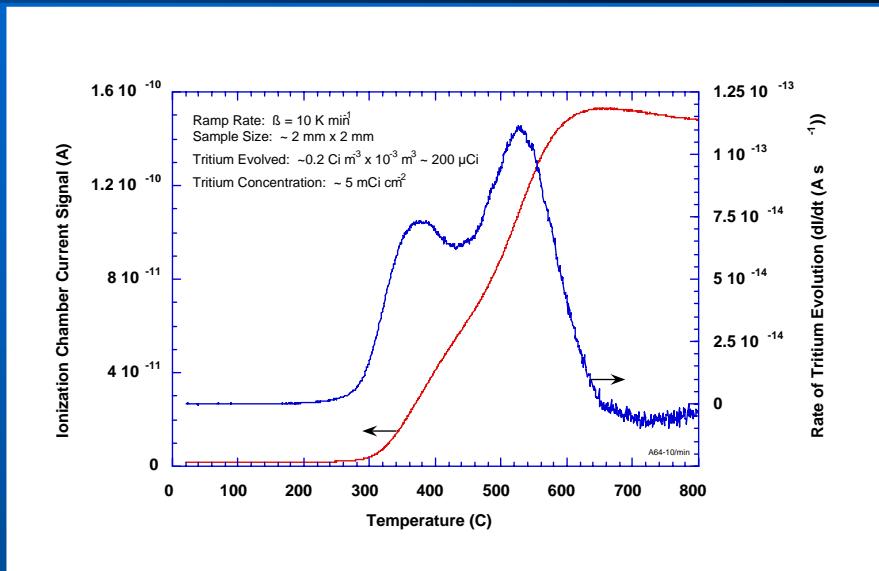


Tritium Effusion Monitor



Tritium Effusion

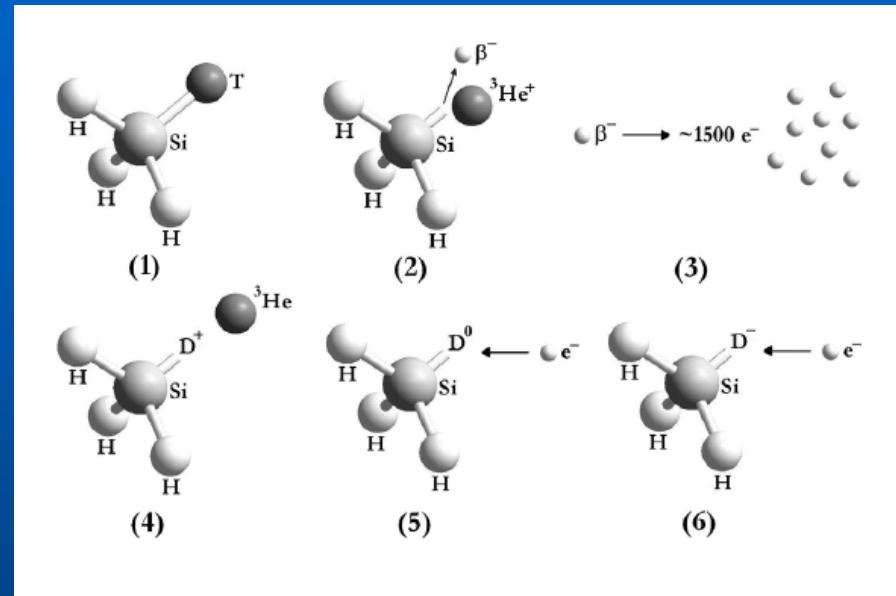
- Tritiated amorphous silicon
 - No tritium evolution at room temperature
 - Characteristic peaks observed at temperatures above the film growth temperature
 - Lower temp peak: higher hydrides SiH_x
 - Higher temp peak: mono-hydride SiH
- Tritiated carbon nanotubes
 - Tritium exposure:
 - 100 bar at 100 °C for 3 days
 - Concentration:
 - Atomic: 1.9%
 - Weight: 0.5%.
 - Gaussian deconvolution:
 - Peaks at 240 °C and 500 °C
 - High temp peak: chemisorbed T
 - Low temp peak: physisorbed T



- Purified Single Walled Carbon Nanotubes (SWNT)
- ~25 μm paper-like film
- Surface Area: 1500 m²/g
- Density: ~0.9 g/cm³.

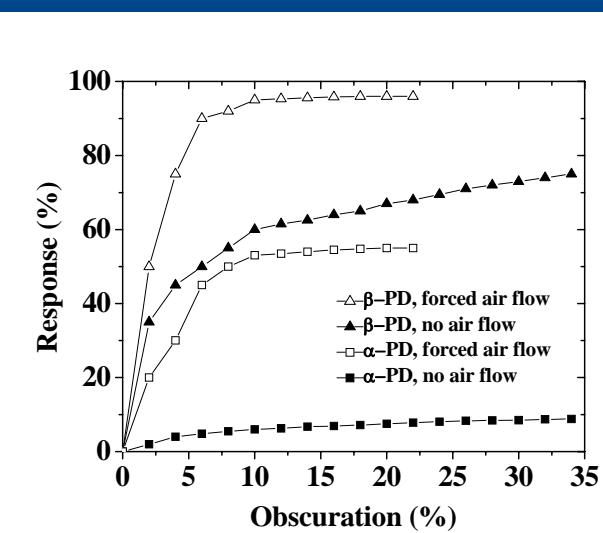
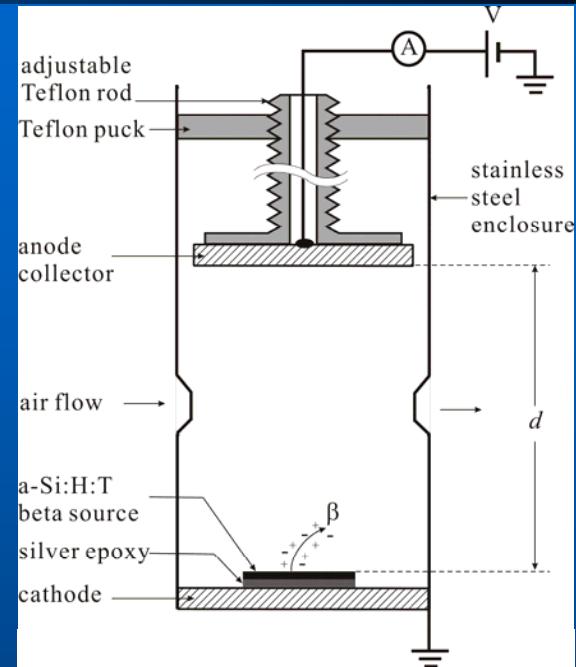
Defect Dynamics

- **Hydrogenated amorphous silicon solar cells**
 - Staebler-Wronski effect
 - Formation of Si-dangling bonds upon light exposure
 - Drop in efficiency
- **Tritiated amorphous silicon**
 - Defined rate of tritium decay, hence formation of Si-dangling bonds
 - Can study samples under defined conditions (no light exposure)
- **Dynamic defect model**

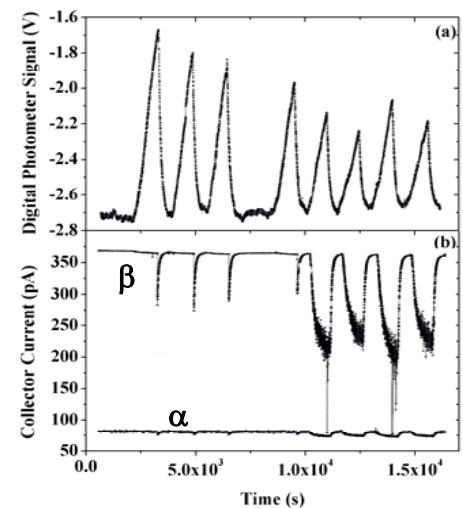


Beta Source Particle-Smoke Detector

- Tritium beta source instead of traditional alpha source
 - No gamma emission (as in Am-Be alpha source)
 - Provides bipolar and unipolar regions in the detector
 - Higher absolute current signal
 - Higher sensitivity
 - Several to forty fold more responsive than alpha based detectors
 - Functions like a dual detector (ionization and photoelectric detectors)
 - Smouldering fires
 - Open flame fires



Liu, Alvarez-Ossa, Kherani,
Zukotynski, Chen,
IEEE Sensors J. 7 (2007) 917.



Summary

- **Tritium a micro-power source**
 - Radio-Isotope Micropower Sources (RIMS) is an active area of R&D
 - Renewed interest is motivated by continual miniaturization of electronic and electromechanical devices with concurrent reduction in power requirements
 - Tritium an amenable radioisotope given its properties and availability
- **Tritium a powerful diagnostic for hydrogen-material studies**
 - Ease of experimentation given hydrogen is pervasive
 - Unparalleled sensitivity under “non-vacuum” conditions
 - Fundamental studies

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- Natural Sciences & Engineering Research Council of Canada
- Defense Advanced Research Project Agency
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- Ontario Power Technologies
- National Sciences Foundation
- BetaBatt
- University of Rochester
- Rochester Institute of Technology
- University of Pittsburgh
- University of Toronto